

Ultrafast Manipulation of Self-Assembled Form Birefringence in Glass

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Ultrashort pulse lasers have allowed probing of molecular dynamics in real time on the femtosecond time scale,^[1] with exotic behavior ranging from alignment of molecules and clusters,^[2,3] structural deformation,^[4] phase transitions on solid,^[5] and electron localization in magnetic materials.^[6] A recent progress in high power ultrashort pulse lasers has opened new frontiers in physics and technology of light-matter interactions^[7] from X-ray generation,^[9] nuclear fusion,^[10] laser surgery,^[11] integrated and fiber optics,^[12,13] optical data storage,^[14,15] to 3D micro- and nano-structuring.^[16–18] An intriguing phenomenon that currently attracts a lot of interest is the self-assembly of periodic nanostructures in the direction perpendicular to the light polarization.^[19,20] Uniaxial birefringence observed after femtosecond laser irradiation of silica glass^[21] has been explained by induced nanogratings and referred as self-assembled form birefringence.^[22,23] Self-organization process has been interpreted in terms of the interference of electron plasma waves resulting in electron concentration modulation, followed by freezing of the interference pattern by structural change in glass. However, the mechanism including dynamics of self-organized nanostructures formation is still not fully understood. Recently, a double-pulse pump-probe configuration was used to enhance ablation in fused silica^[24] and silicon.^[25] In similar experiments molecular ensembles with an oriented angular momentum were produced.^[26] Here, we describe the ultrafast writing dynamics of form birefringence produced by self-organized nanogratings in double pulse experiments. Rewritable five-dimensional (5D) optical data storage using self-assembled form birefringence was demonstrated.

In the experiments a laser beam was equally split by a polarizing beam splitter (BS1) (Figure 1a). The polarization of one of the beams was then rotated by a half-wave plate to be orthogonally polarized with respect to the other arm. The time delay, τ_{delay} , between orthogonally polarized pulses was varied using an optical delay line. Finally both beams were recombined on the second polarizing beam splitter (BS2). The laser beam was focused via a microscope objective (Nikon; LU Plan Fluor, 100×0.90 N.A.) at a depth of about $50 \mu\text{m}$ below the surface of silica glass sample. The pulse energy was about $1.0 \mu\text{J}$ and the beam power measured after microscope objective was independent on the orientation of light polarization. The repetition rate of the laser was set to 250 kHz corresponding to an interpulse interval τ_{int} of $4 \mu\text{s}$ (Figure 2a). A series of dots were written in fused silica using the orthogonally polarized double-pulse beam with different time delays τ_{delay} . After writing, the modified structures were inspected using optical and polarization (Polscope, CRI) microscopes.

In the experiments with singly polarized pulses one of the beams was blocked (Figure 1b) and a series of dots were written in the glass sample. As a result, the periodic nanostructure was induced in the orthogonal direction to the light polarization (Figure 1a).^[19] Such a nanograting structure, consisting of periodic oxygen defect regions, is responsible for form birefringence.^[22,23] The direction of the slow axis of birefringence (a_{slow}), which is always perpendicular to the writing light polarization, can be controlled by rotating the polarization (Figure 1b). In the next experiment a series of dots were written by two trains of pulses ($250\,000$ pulses in each train) with orthogonal polarizations (Figure 1c). Each train was produced by blocking one of the beams for 1 second. The characterization of irradiated zones with a polarization microscope revealed that nanograting orientation is only defined by the last pulse train, meaning that birefringence is rewritable (Figure 1c). Erasure of the nanostructure requires sufficiently high temperatures as the induced oxygen defects are maintained up to the glass transition temperature T_g of $\sim 1200^\circ\text{C}$.^[27] The polarization-dependent nanostructure can act as a bit of rewritable optical memory, which would possess extremely high thermal stability in contrast to currently used rewritable memories based on phase transition.

In order to investigate nanograting erasure dynamics we performed time-resolved (with resolutions $70 \pm 40 \text{ fs}$) experiments with cross-polarized double pulses. A series of dots was written with different delay between two perpendicularly polarized pulses. After irradiation the azimuth angle of birefringence was characterized (Figure 2). In double pulse experiments for delay

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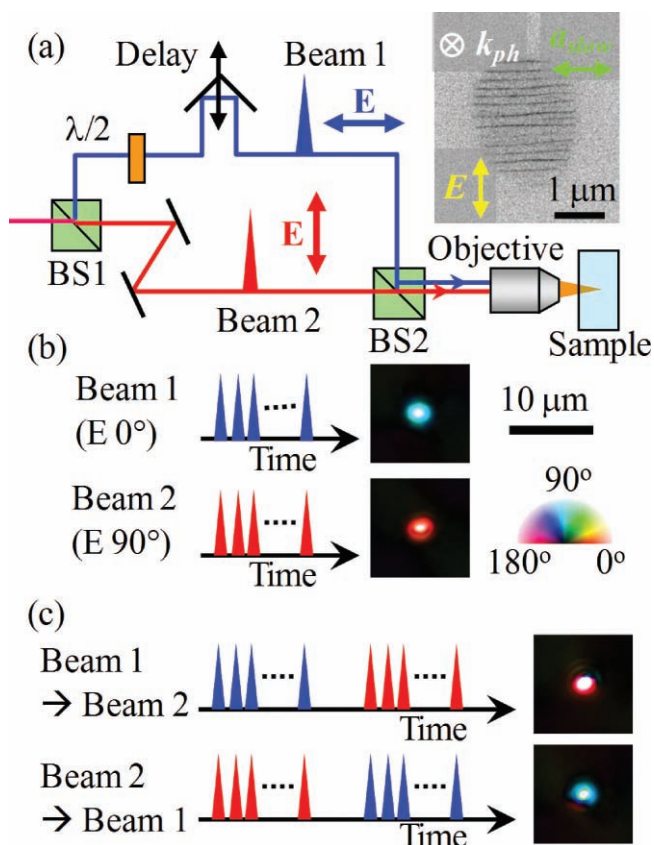


Figure 1. (a) Orthogonally polarized double pulse experiment setup: polarizing beam splitters (BS1, BS2), half-wave plate ($\lambda/2$), optical delay line (Delay), microscope objective (Objective). (Inset) Backscattering electron image of femtosecond laser induced self-organized nanograting, slow axis of birefringence a_{slow} is perpendicular to the laser polarization E (k_{ph} indicates light propagation direction). (b) Pulse diagrams of single polarization ($E = 0^\circ$ and $E = 90^\circ$) experiments with corresponding images of written dots taken with polarization microscope (pseudo color indicates direction of slow axis of birefringence as indicated in polar legend). (c) Rewriting of nanograting by successively irradiating single spot with orthogonally polarized trains of pulses.

times below 200 fs the azimuth angle of the slow axis asymptotically approached value observed in single polarized beam experiment (Figure 2c). Over 200 fs the azimuth angle was defined solely by the last pulse polarization. Based on the autocorrelation function $A(\tau) = \int_{-\infty}^{+\infty} E_V(t) E_H(t - \tau) dt$, where $E_V(t)$ and $E_H(t)$ are the electric field of orthogonally polarized double pulses, the time scale of the modification of azimuth angle corresponds to the pulse width inside fused silica (Figure 2c). The rapid change of the azimuth angle demonstrates that the nanograting direction is defined only during light interaction with plasma and the self-organization process is of electronic origin. Formation of the nanograting itself, however, extends to ps scale and cannot be observed in the current experimental conditions.

Despite the fact that the pulse energy and pulse duration of the orthogonally polarized double pulses were the same, the asymmetric evolution of retardance was unambiguously observed in the double pulse experiment (Figure 2d). A small difference in the retardance also exists between the orthogonally

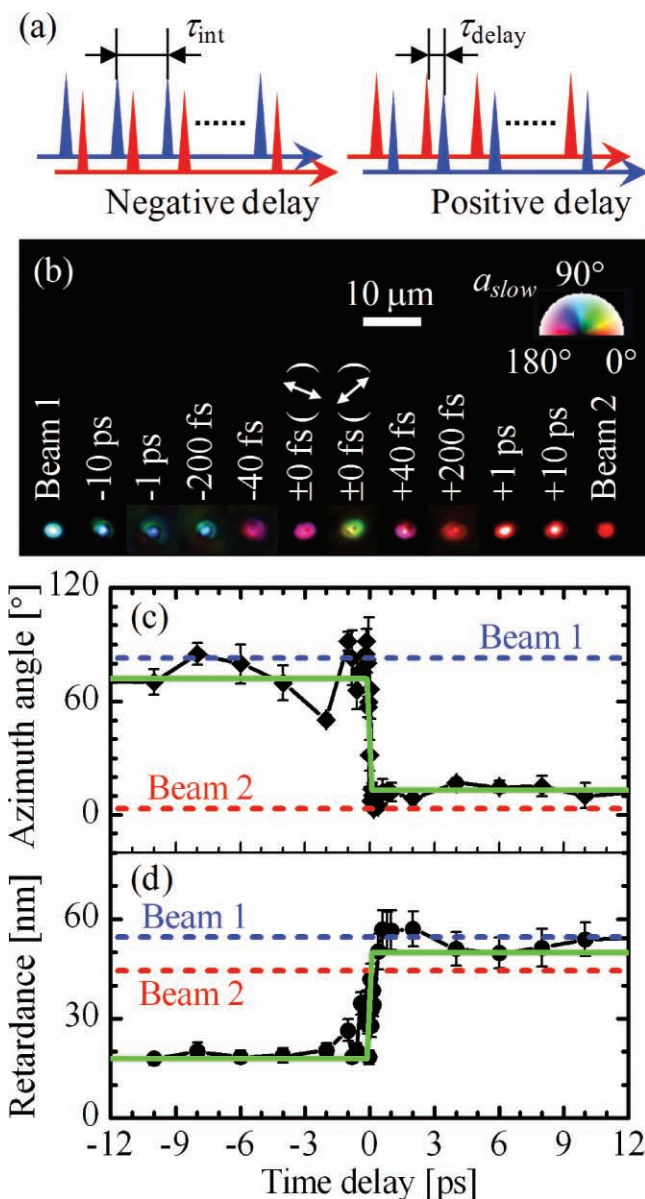


Figure 2. Femtosecond time-resolved observations of localized birefringence manipulation. Pulse diagrams of double pulse experiments (a). τ_{int} and τ_{delay} indicate an interpulse time and a time delay between double pulses, respectively. Characteristic microscopy images of localized birefringence (b) taken with polarization optical microscope (pseudo color indicates direction of the slow axis, see polar legend), corresponding plots of the azimuth angle (c) and the retardance (d) versus delay time τ_{delay} between pulses. For eye guidance azimuth angle and retardance of the orthogonally polarized single beams (Beam 1: $E = 0^\circ$ and Beam 2: $E = 90^\circ$) are indicated by blue and red dashed lines, respectively. Green curves in (c) and (d) indicates the Gaussian autocorrelation function and Gaussian integral respectively.

polarized single beams, but this is several times smaller than in the double pulse case. The explanation of observed asymmetric evolution could be as following. The first pulse of double pulse creates the nanograting and the second pulse with the orthogonal polarization overwrites it with a new one. When the next

double pulse arrives, the first pulse will erase the nanograting left from the last pulse of the previous double pulse. Let us assume that horizontal and vertical polarization produces different heating. Namely horizontal polarization produces less heating than vertical. In this case the first pulse with the horizontal polarization from the second double pulse may *not* erase the nanograting produced by the second pulse with vertical polarization from the first double pulse. So, the nanograting (and retardance) grows from one double pulse to another. On the other hand, when the pulse sequence is reversed, the vertical polarization from the second double pulse will *erase* the nanograting produced by the second pulse with horizontal polarization from the first double pulse. So, the nanograting (and retardance) will not grow. Indeed, the growth of retardance in double pulse experiments can be fitted well by the integrated Gaussian function, assuming the different thermal accumulation ideally describes a Gaussian temporal distribution (Figure 2d). This phenomenon indicates that the induced birefringence depends on the light polarization and could be related to the pulse front tilt.^[28,29] Since the anisotropic sensitivity of an isotropic medium cannot be defined by the material structure or its interfaces, the experimental results can be derived from the intrinsic anisotropy of the light-matter interaction involving intense ultrashort light pulses with a tilted intensity front. Such heating anisotropy in a homogeneous medium could be interpreted in terms of plasma inhomogeneity originating from the mutual orientation between a light polarization and a pulse front tilt. Indeed we have also observed a weak dependence of the absorbed light power and strong dependence of the hot plasma emission on the light polarization. This reveals that the same amount of absorbed energy can result in different excitations and material modifications. Deeper investigation of this phenomenon will be reported elsewhere.

The oxygen mobility in a glass matrix is generally very slow compared with the optical phenomena. Assuming that the temperature of the focal spot reaches $T = 3000$ °C, the oxygen diffusion length was calculated by Fick's law $L_D = \sqrt{D_n t}$, $D_n = D_0 \exp(-Q/RT)$, where $D_0 (= 2.6 \times 10^{-4} \text{ m}^2 \text{ s}^{-1})$ is the maximum diffusion coefficient (at infinite temperature), Q is the activation energy ($= 454 \text{ kJ mol}^{-1}$), and R is the gas constant. Since the width of the oxygen defect regions in nanograting structure was ~ 20 nm, the diffusion time was estimated to be at least $40 \mu\text{s}$.^[30]

In order to reveal the growth mechanism of the anisotropic nanostructure, we have investigated the evolution of birefringence varying repetition rate (or the interpulse time τ_{int}) and exposition (or the number of pulses, N_{pulse}) at a pulse energy of $1.0 \mu\text{J}$ in a single beam configuration (Figure 1b). The evolution of the retardance (δ) with exposition time was then measured at different interpulse intervals τ_{int} (4, 8, 40, and $400 \mu\text{s}$) (Figure 3). Only stress birefringence caused by local heating was observed for exposures below 100 pulses. While form birefringence induced by sub-wavelength periodic structures was detectable only after more than 100 pulses. Induced form birefringence showed tendency to saturate after several hundreds of pulses that could be explained by total depletion of oxygen inside nanograting corrugations. The optimal interpulse time τ_{int} to achieve highest retardance value was of $40 \mu\text{s}$, which also corresponds to oxygen diffusion time mentioned above.

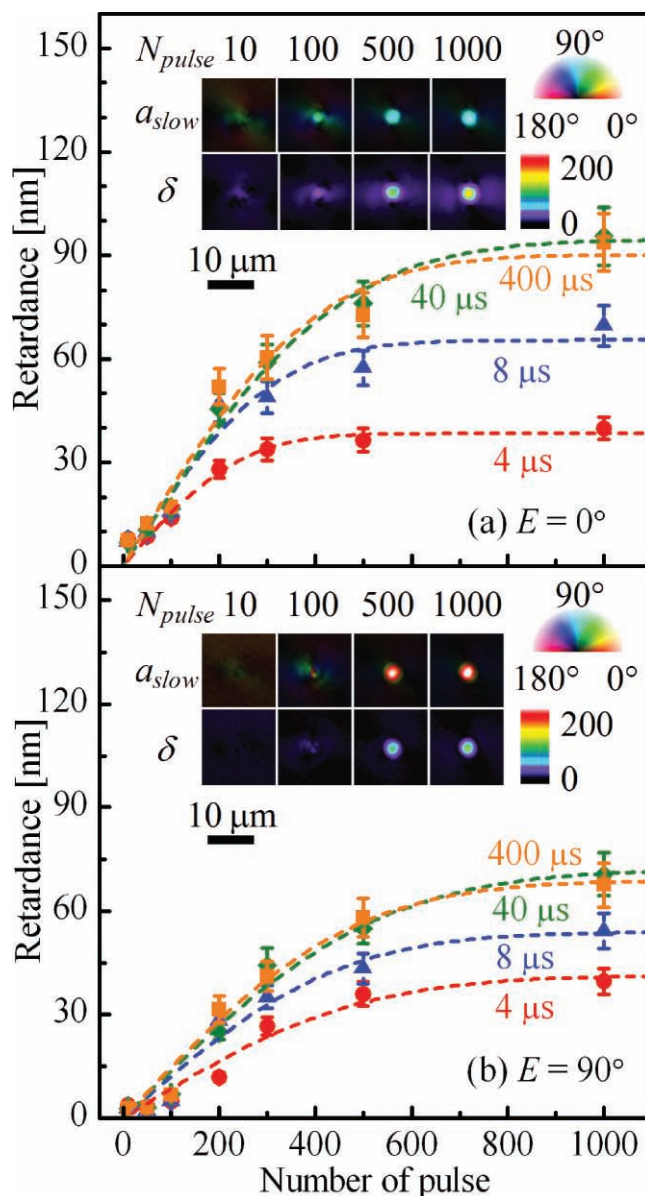


Figure 3. Evolution of the optical anisotropy for two orthogonal polarizations (a) $E = 0^\circ$ and (b) $E = 90^\circ$ versus the number of pulses with different τ_{int} (4 μs , 8 μs , 40 μs , 400 μs). (Insets) Microscopy images taken with a polarization microscope indicating the orientation of the slow axis (a_{slow}) and the retardance value (δ) induced by various numbers of pulses at $\tau_{\text{int}} = 40 \mu\text{s}$.

Alternatively, lower retardance value for $\tau_{\text{int}} < 40 \mu\text{s}$, could be explained by thermal accumulation,^[31] which deteriorates the quality of the self-assembled nanostructure. These results obviously indicate that the evolution of retardance can be controlled as a function of interpulse time. Furthermore, in spite of the same pulse energy, the evolution of retardance is obviously different depending on the polarization direction, especially for the longer interpulse time corresponding to the lower thermal accumulation effect. For an interpulse time of $\tau_{\text{int}} = 4 \mu\text{s}$ and exposition times below 100 pulses, the growth speed of the retardance for two perpendicular polarizations $E = 0^\circ$

and 90° was estimated to be 3.6×10^{-2} and $1.5 \times 10^{-2} \text{ nm } \mu\text{s}^{-1}$, respectively. The lower saturation value of the retardance produced by the vertically polarized pulses compared with the horizontal polarization corresponds to the temporal variation of the retardance in double pulse experiments (Figure 2d). Such polarization dependence could be interpreted in terms of the difference in the internal stress distribution due to local heating.

We propose the following explanation of the dynamics of anisotropic nanostructure self-organization. Once a high free-electron density is produced by multiphoton and avalanche ionizations, periodic modulation of the electron concentration appears within the pulse width, resulting from plasma wave interference. Most electrons are then trapped into deep levels and form the well-known E' centers within a time scale of $\sim 15 \text{ ps}$.^[32] The electron density modulation is then frozen into permanent material modification. Multiple pulses gradually improve this modulation until total reduction of the oxygen due to diffusion is reached.

Apart from fundamental understanding, we experimentally demonstrate an application of photo-induced nanograting in the *rewritable five-dimensional optical storage* by use of liquid-crystal technology for writing and reading the data. For the recording, a reflection type of spatial light modulator based on liquid-crystal-on-silicon technology (Hamamatsu Photonics; LCOS-SLM) was used to modulate the spatial phase distribution of the writing beam. By this technique, a single laser beam with the polarization direction controlled with a $\lambda/2$ wave plate can be split into 100 beams of equal pulse energy ($1.0 \mu\text{J}$) via holographic patterns provided by the LCOS-SLM. To demonstrate the potential of this technology we produced the “world map” within a $3.4 \times 1.8 \text{ mm}$ square inside fused silica **Figure 4(a)**. Printing of this image takes only about 20 minutes. Reading of the recorded information was realized with the polarization optical microscope. Basic working principle of this microscope is the following, a nearly monochromatic (wavelength: $\sim 550 \text{ nm}$, bandwidth: $\sim 30 \text{ nm}$) circularly polarized light illuminates the sample, then it is passed through a liquid crystal compensator, which modulates light polarization, and fixed analyzer before reaching a detector. As a result the “pointillism” composed of multi-colored dots corresponding to different slow axis orientation of the form birefringence was clearly observed (Figure 4b). Simultaneously the phase retardation can be also read out (Figure 4c). Due to the slight configuration errors in writing or the detection systems and limited sensitivity of CCD detector used for reading, the resolutions of the azimuth angle and the phase retardation were respectively less than 4.7° and 5 nm . By applying these techniques we have demonstrated the rewritable optical data storage in “five dimensions” (3 coordinates, the slow axis direction, and retardance) with a 300 Gbit cm^{-3} capacity corresponding to the 10 times of the usual 12 cm BlueRay disk capacity (see Supporting Information, Movie 1). This technique, being simple and easily available, has the advantage over other types of optical memory, e.g., holographic memory, fluorescence 3D memory, and spectra hole-burning (SHB) memory.^[15,33,34]

In summary, we have experimentally observed ultrafast writing dynamics of form birefringence. The dynamics of the anisotropic response indicates that the plasma interference

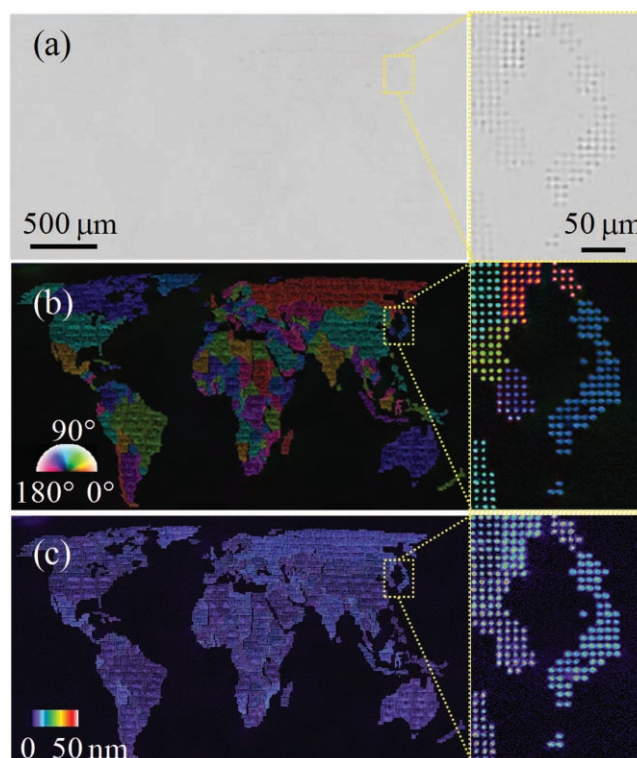


Figure 4. Images of the “Small World Map” taken with optical (a) and polarization (b – azimuth angle, c – retardance) microscopes. The structure was printed in silica glass using femtosecond laser beam modulated with LCOS-SLM. Actual size of the structure is $3.4 \text{ mm} \times 1.8 \text{ mm}$. The highly magnified images of the marked area are shown on the right.

effect occurs within a time scale of $\sim 150 \text{ fs}$ followed by the formation of oxygen vacancies during the plasma lifetime. Self-organization of defect structures gradually evolves during multiple pulse irradiation. We anticipate that these results will motivate the development of rewritable 5D optical storage devices.

Experimental Section

Encoding of optical anisotropy and medium: The experiments were performed using a mode-locked, regeneratively amplified Ti:Sapphire laser system (Coherent; RegA 9000), operating at 800 nm with 70 fs pulse duration. The interpulse time τ_{int} and the number of pulses N_{pulse} were controlled by field programmable gate array (National Inst.; FPGA module 7811R) produced the trigger pulses. Samples for the experiments were prepared from commercially available synthetic fused silica (Shin-Etsu Quartz: VIOSIL-SQ) containing approximately 500 ppm OH . Sample position control was realized with 3-axial computer controlled high precision mechanical stage.

Holographic encoding: Multiple beam spots of femtosecond laser pulses were generated from one beam whose phase distribution was modulated by a computer generated hologram (CGH) displayed on a spatial light modulator (SLM). The CGHs for the spatial phase modulation were created by a Fourier repetition method. Instant large-area processing can be realized switching CGHs on a spatial light modulator in conjunction with synchronized sample position control.

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